REMARKS

Claims 1-62 and 81 are pending in this application. Claims 63-80 have been canceled. Claims 1, 2, 11, 12, 20, 23, 30, 32, 41, 42, 50, 53, 60 and 81 have been amended for reasons unrelated to patentability, without prejudice and without conceding to the Examiner's characterizations. Each of these claims have been rejected, and Applicant traverses each rejection as follows.

35 U.S.C. 112, first paragraph

WRITTEN DESCRIPTION

Claim 1-12, 14-42, 44-62 and 81 are rejected under 35 U.S.C. 112, first paragraph, for written description. The Examiner stated that "the expression sulfur derivatives, does not meet the written description requirement as one of ordinary skill in the art could not recognize or understand the compounds [from] mere recitation of R being organic radical in the organic sulfide category and to the nature of inorganic in inorganic sulfites, metabisulfites...Applicant[']s claimed expression represents only an invitation to experiment regarding possible compounds suitable as sulfur derivatives, which can be used in the composition for absorbing irritants in the skin and delivering sulfur." Applicant traverses this, and notes that Applicant used a term "sulfur derivatives" that is known to one of ordinary skill in the art. Exhibit A lists 82 U.S. patents which use the term "sulfur derivative." U.S. patents are presumptively valid and therefore, point to the fact that one of ordinary skill in the art understands "sulfur derivative" and is sufficiently descriptive to meet 35 U.S.C. 112 written description. The Examiner has offered no proof that this is merely "an invitation to experiment" and does not allegedly meet the written description requirement. Applicant invites

the Examiner to cite reasons in support of this position as is required by MPEP § 2163.04. In the absence of such evidence, Applicant requests that this rejection be removed.

ENABLEMENT

Claims 1-12, 14-42, 44-62 and 81 have been rejected under 35 U.S.C. § 112, first paragraph for lack of enablement. The Examiner asserts that "only specific concentration[s] of sulfur can be used for the claimed method without causing toxicity, and also the three sulfur derivatives cannot be used for the claimed method." Applicant traverses this rejection. Applicant is not required to describe all actual embodiments. SRI Int'l v. Matsushita, 775 F. 2d 1107 (Fed. Cir. 1985). Therefore, Applicant is not required to list each specific concentration since one of ordinary skill in the art would be able to practice this invention.

The Examiner argues that "hydrogen sulfide is a poisonous gas with a characteristic smell of rotten eggs . . . sulfuric acid is corrosive to all body tissues . . . sulfur trioxide as irritant and corrosive to mucous membranes and at the low concentration of 1 ppm may cause coughing, choking and severe discomfort." However, Applicant notes that the claimed composition comprises more than any one of these compounds alone; in combination, chemicals may behave differently than alone. The Examiner has offered no proof that the claimed composition is not enabled, merely that individual ingredients have these properties alone, which is not Applicant's invention. The Examiner has not met the burden of providing specific technical reasons under MPEP §2164.04.

Further, the Examiner argues "that rising [sic] 6% sulfur in the base petrolatum is effective and higher concentration of sulfur is toxic." Six percent sulfur in petrolatum alone is not Applicant's invention, and thus is not relevant to the present application. Moreover, the Examiner's contention that the use of more than 6% sulfur is toxic is simply wrong. Products

having more than 6% sulfur have been used for many years, and have been specifically approved by the U.S. Food and Drug Administration ("FDA"). The FDA publishes acceptable concentration ranges of sulfur in topical drug products as "3 to 10 percent." See 21 C.F.R. §333.310 from 50 FR 2172, a copy of which is attached as Exhibit B. If the Examiner is prepared to dispute the wisdom of the FDA in approving products containing as much as 10% sulfur, she should so state, and provide evidence that the FDA's actions have been in error. Absent such proof, one of ordinary skill in the art would know that these are acceptable ranges and thus the requirements of 35 U.S.C. §112, ¶ 1 are fulfilled. Therefore, this rejection should be removed.

The Examiner sets forth eight factors "to support a determination that a disclosure does not satisfy the enablement requirement and whether any necessary experimentation is undue." The Examiner asserts that undue experimentation is required in the present claims. Applicant respectfully submits that so long as the experimentation required for practicing the invention is routine, the extent of such experimentation is immaterial to § 112 requirements. The Federal Circuit supported Applicant's view in *In re Wands*, 8 U.S.P.Q.2d 1400, 858 F.2d 731 (Fed. Cir. 1988) which stated the test whether experimentation required to practice an invention is undue,

> is not merely quantitative, since a considerable amount of experimentation is permissible, if it is merely routine, or if the specification in question provides a reasonable amount of guidance with respect to the direction in which the experimentation should proceed.
> *In re Wands*, 8 U.S.P.Q.2d 1400, 858 F.2d 731 (Fed. Cir. 1988)

In order to practice the *Wands* invention, extensive (but not undue) experimentation was required, but this did not preclude a finding that the *Wands* claims were enabled. Therefore, since Applicant's claims do not require undue experimentation, Applicant's claims are still enabled. The specification teaches what the invention is and how to use it, so that one skilled in the art can practice the invention as claimed without the burden of undue experimentation and §

112 is satisfied. If the Examiner believes that it would be qualitatively un-routine to duplicate the Applicant's invention based upon the specification, Applicant invites the Examiner to cite evidence or offer a declaration to this effect. Based on the present record, Applicant asserts that this rejection should be removed.

35 U.S.C. § 112, second paragraph

INDEFINITENESS

Claims 1-62 and 81 are rejected under 35 U.S.C. §112, second paragraph, as "being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention." The Examiner argues that " 'comprises one or more of the group consisting of' for defining the Markush group is indefinite." Applicant has amended claims 1, 2, 11, 12, 20, 23, 30, 32, 41, 42, 50 53, 60 and 81, for reasons unrelated to patentability, to read, "selected from the group consisting of." MPEP 2173.05(h). Applicant requests that this rejection be removed.

The Examiner argues that " 'cationic sulfur compounds' is without metes and bounds." Applicant traverses this rejection. "Cationic sulfur compounds" is known to one of ordinary skill in the art. Exhibit C is a U.S. patent which uses the term "cationic sulfur compounds." U.S. patents are presumptively valid and therefore, point to the fact that one of ordinary skill in the art understands "cationic sulfur compounds" and the term is sufficiently definite to fulfill 35 U.S.C. 112, second paragraph requirements. Applicant requests the removal of this rejection.

Also, the Examiner states that "claims 7-8, 13, 168, 21, 24, 26, 37, 37-39, 43, 46-48, 51 and 54 are unclear as to applicant's intent. The claims recite "comprises" followed by one compound." Applicant does not understand part of the Examiner's rejection of claim

168 because there is no pending claim 168. Otherwise, Applicant traverses this rejection. "Comprising" or comprises is specifically addressed in MPEP 2111.03 with a clear definition set forth and therefore it is not unclear. Applicant requests removal of this rejection.

35 U.S.C. § 102

The Examiner rejected claims 1-15, 20, 30-36, 41-45, 50, 56, 60 and 81 under section "102(b) as being anticipated by sulfur revisited article" by Lin et al in American Journal of Dermatology. Applicant traverses this rejection. Nothing in this office action discusses how and where Lin anticipates each and every claim limitation.

Table IV is cited because the Examiner alleges "[b]entonite reads on the claimed clay," however, the compositions in Table IV with the bentonite do not also include sulfur and one or more sulfur derivatives and, therefore, do not anticipate the claims. Then, the Examiner cites Table II, we believe Table III what was meant by the Examiner. However, nothing in Table III anticipates "absorbing irritants in the skin and delivering sulfur to skin." Lin does not teach all of the claim limitations (e.g. high sorption bases with sulfur or one or more sulfur derivatives) and therefore, Lin does not anticipate the claims and the rejection should be removed.

35 U.S.C. § 103

Applicant acknowledges the reminder from the Examiner regarding section 103(a).

"Claims 1-62 and 81 are rejected under 35 U.S.C. 103(a) as being unpatentable over the combination of Lin et al article cited in 102 rejection and U.S. Patent No. 4,388,301 ('301) and Skin care and cosmetic ingredients dictionary, page 317 (1994)." Applicant traverses this rejection. Applicant reasserts its arguments for the §102 rejection. The Examiner has not met his

burden since no rationale was provided for in the Lin reference (supra). Therefore, the rejection should be removed.

Further, the Examiner notes that U.S. Patent No. 4,388,301 ("'301 Patent") "treating acne using poly-sulfide compounds which is claimed in the instant application as the sulfur derivative along with clays and silica." Applicant notes that the pending claims do not claim methods of treating acne. Additionally, the '301 Patent does not teach the use of sulfur, and Applicant's claimed methods are used to deliver sulfur to the skin. It would not be obvious to use the '301 Patent for Applicant's different methods.

Additionally, the Examiner notes "[g]ums are used as gelling agents or thickeners in the formulations." Applicant does not find any suggestion to use gums with Lin and the '301 Patent. Neither Lin nor the '301 Patent mention thickeners or gelling agents as being advantageous in their inventions. Therefore, the Examiner has not found evidence of each of Applicant's claim elements and has failed to meet the burden for an obviousness rejection. Applicant respectfully requests removal of this rejection.

CONCLUSION

Applicant respectfully submits that the application is in condition for allowance.

Applicant does not believe any additional fee is required for this Response and Request for Reconsideration, however, in the event any additional fee is required or any overpayment credit is due, the Commissioner is hereby authorized to charge Deposit Account No. 18-0586.

I hereby certify that this paper and the papers referred to herein as being transmitted, submitted, or enclosed herewith in connection with U.S. Serial No. 10/022,482 is/are being facsimile transmitted to the United States Patent and Trademark Office fax number 703 872 9306 on the date shown below.

Maryellen Feehery

September 16, 2003
Date of Facsimile Transmission

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EXHIBIT A

USPTO PATENT FULL-TEXT AND IMAGE DATABASE

Searching 1976 to present...

Results of Search in 1976 to present db for:
"sulfur derivative": 82 patents.
Hits 1 through 50 out of 82

Final 32 Hits
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Refine Search "sulfur derivative"

	PAT. NO.	Title
1	6,567,625	Image forming apparatus and process cartridge with delayed rotation of photosensitive member
2	6,555,163	Developing roller and method of producing the same
3	6,528,558	Flame retardation of polymeric compositions
4	6,525,072	Geometrically restricted 2-indolinone derivatives as modulators of protein kinase activity
5	6,471,628	Developing roller with porous surface
6	6,461,674	Developing roller and method of producing the same
7	6,369,095	Indole-3-carbinol (13C) derivatives and methods
8	6,344,523	Reduced temperature curing of acetylenic polymers
9	6,169,181	Compounds useful to treat retroviral infections
10	6,150,395	Indole-3-carbinol (I3C) derivatives and methods
11	6,096,811	Modifying agents for polyolefins
12	6,063,932	Process and intermediates for the preparation of oxazoline derivatives
13	6,008,376	Aminohydroxylation of olefins with tert-alkyl sulfonamides
14	6,005,103	Pyrone derivatives as protease inhibitors and antiviral agents
15	6,001,868	Indole-3-carbinol (I3C) derivatives and methods
16	6,001,782	Metal overbased fatty amines further derivatized to contain covalently bound sulfer and/or phorphorus useful as antiwear/extreme pressure additives
17	5,967,134	Liquid gas grill apparatus and method

18 5,962,291 Metal dependent catalytic antibodies and method for producing the same
19 5,905,106 Composition that is extrudable and curable in air
20 5,879,805 Gas phase polymerization of vinylpolybutadiene
21 5,852,195 Pyranone compounds useful to treat retroviral infections
22 5,808,062 Pyrone derivatives as protease inhibitors and antiviral agents
23 5,801,274 N-›mercaptoacyl(amino acid or peptide)! compounds and S-lipophilic aliphatic carbonyl derivatives thereof as antihypertensives
24 5,795,927 Color stable wrinkle finish epoxy powder coating
25 5,763,014 Liquid applied waterproofing
26 5,759,726 Electrographic photosensitive member
27 5,681,797 Stable biodegradable lubricant compositions
28 5,674,864 N-substituted derivatives of .alpha.-mercapto alkylamines, their preparation process and the intermediates obtained, their use as medicaments and the compositions containing them
29 5,591,891 N-[Mercaptoacyl (amino acid or peptide)] compounds and S-lipophilic aliphatic carbonyl derivatives thereof as antihypertensives
30 5,536,730 Imidazonaphthyridine derivatives
31 5,484,924 Imidazonaphthyridine derivatives
32 5,468,756 Imidazonaphthyridine derivatives
33 5,424,344 Flame retardant polyamide compositions
34 5,410,071 Process for sulfur-containing derivatives of hydroxyphenylbenzotriazoles
35 5,387,718 Method of manufacturing alkylphenyl alkyl ethers or alkylphenyl alkyl thioethers
36 5,380,786 Polyvinyl chloride blends having improved physical properties including low temperature brittleness
37 5,364,859 Imidazonaphthyridine derivatives
38 5,346,760 Composite material based on rubbers of the silicone type and of the ethylene-propylene copolymer or terpolymer type
39 5,342,843 Thienoimidazoppyridone derivatives
40 5,334,736 Functionalizing carbohydrate derivatives by base-induced .beta.-eliminatiom forming bioactive derivatives containing hydroxy-diene subunits
41 5,286,589 Electrophotographic photosensitive member
42 5,273,578 Light-modifying composition
43 5,221,667 Renin inhibiting peptides having an .alpha.-heteroatom amino acid at the P.sub.3 position
44 5,197,399 Pulse combusted acoustic agglomeration apparatus and process
45 5,190,974 N-substituted derivatives of .alpha.-mercapto alkylamines, their preparation process and the intermediates obtained, their use as medicaments and the compositions containing them
46 5,153,269 Thermoplastic elastomer blends of a polyvinyl chloride-acrylate copolymer and a cured acrylate elastomer
47 5,126,485 Process for the hydrogenation of halogenonitro-aromatic compounds in the presence of a sulfur-containing compound

48 5,105,011 T Process for the hydrogenation of halogenonitro-aromatic compounds in the presence of an iodide

49 5,055,515 T Flexible overpolymers of vinyl chloride polymers on ethylene copolymers

50 4,997,979 T Process for the preparation of alkaline phenylpyrovate

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USPTO PATENT FULL-TEXT AND IMAGE DATABASE

Searching 1976 to present...

Results of Search in 1976 to present db for:
"sulfur derivative": 82 patents.
Hits 51 through 82 out of 82

Prev. 50 Hits
Jump To

Refine Search "sulfur derivative"

PAT. NO.	Title
51 4,983,665	Flexible blend compositions based on overpolymers of vinyl chloride polymers on ethylene copolymers
52 4,963,418	Thermo-shrinkable polyester type film and tube and processing method for preparing the tube
53 4,937,291	Thermoplastic elastomer blends of a polyvinyl chloride-acrylate copolymer and a crosslinked nitrile elastomer
54 4,935,468	Thermoplastic elastomer blends of a polyvinyl chloride-acrylate copolymer and a cured acrylate elastomer
55 4,925,979	Flavone carboxylic acid derivatives
56 4,831,052	Flavone carboxylic acid derivatives
57 4,680,297	Tricyclic positive inotropic agents
58 4,581,336	Surface-modified electrodes
59 4,576,809	Preparation of alkali or alkaline earth metal cobalttetracarbonylates and catalysts of carbonylation reactions therewith
60 4,552,740	Process for producing amorphous and crystalline silicon nitride
61 4,536,358	Process for the production of high surface area catalyst supports
62 4,536,312	Sulfurized amine condensation products and lubricant compositions containing same
63 4,496,756	Process for preparing amino acid esters

64 4,410,739 T Preparation of meta-chlorophenols by selective hydrodechlorination of polychlorophenols
65 4,410,738 T Preparation of meta-chlorophenols by selective hydrodechlorination of polychlorophenols
66 4,410,737 T Preparation of meta-chlorophenols by selective hydrodechlorination of polychlorophenols
67 4,380,679 T Hydrogenation of saccharides
68 4,333,770 T Extraction of sucrose from molasses
69 4,330,298 T Reductive pyrolysis method for determining trace sulfur
70 4,329,260 T Integral shaped replication supports
71 4,319,058 T Process for the separation of ethanol from water
72 4,312,678 T Extraction of sucrose from molasses
73 4,255,359 T Non-polluting oxyhydrochlorination process
74 4,243,596 T (5-Nitro-2-furyl)vinylene-2-trimethylammonium bromide and method of preparing same
75 4,238,206 T Using solvents for acidic gas removal
76 4,090,978 T Electrocatalysts and a method for the preparation thereof
77 4,031,292 T Method for the preparation of an electrocatalyst
78 4,016,047 T Separation and recovery of polychlorinated phenols
79 4,000,100 T Thermal and light stabilized polyvinyl chloride resins
80 3,994,950 T Xanthate-Lewis acid complexes
81 3,973,234 T Precision type resistor
82 3,972,732 T Electrochemical cell

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EXHIBIT B

50 FR 2172-01
1985 WL 83812 (F.R.)
(Cite as: 50 FR 2172)

PROPOSED RULES

DEPARTMENT OF HEALTH AND HUMAN SERVICES

21 CFR Part 333

[Docket No. 81N-0114]

Topical Acne Drug Products for Over-the-Counter Human Use; Tentative Final Monograph

Tuesday, January 15, 1985

*2172 AGENCY: Food and Drug Administration.

ACTION: Notice of proposed rulemaking.

SUMMARY: The Food and Drug Adminstration (FDA) is issuing a notice of proposed rulemaking in the form of a tentative final monograph that would establish conditions under which over-the-counter (OTC) topical acne drug products are generally recognized as safe and effective and not misbranded. FDA is issuing this notice of proposed rulemaking after considering the report and recommendations of the Advisory Review Panel on OTC Antimicrobial (II) Drug Products and public comments on an advance notice of proposed rulemaking that was based on those recommendations. This proposal is part of the ongoing review of OTC drug products conducted by FDA.

DATES: Written comments, objections, or requests for oral hearing on the proposed regulation before the Commissioner of Food and Drugs by May 15, 1985. New data by January 15, 1986. Comments on the new data by March 17, 1986. These dates are consistent with the time periods specified in the agency's revised procedural regulations for reviewing and classifying OTC drugs (21 CFR 330.10).

ADDRESS: Written comments, objections, new data, or requests for oral hearing to the Dockets Management Branch (HFA-305), Food and Drug Administration, Rm. 4-62, 5600 Fishers Lane, Rockville, MD 20857.

FOR FURTHER INFORMATION CONTACT: William E. Gilbertson, Center for Drugs and Biologics (HFN-210), Food and Drug Administration, 5600 Fishers Lane, Rockville, MD 20857, 301-443-4960.

supplementary information: In the Federal Register of March 23, 1982 (47 FR 12430) FDA published, under § 330.10(a)(6) (21 CFR 330.10(a)(6)), an advance notice of proposed rulemaking to establish a monograph for OTC topical acne drug products, together with the recommendations of the Advisory Review Panel on OTC Antimicrobial (II) Drug Products, which was the advisory review panel responsible for evaluating date on the active ingredients in this drug class. Interested persons were invited to submit comments by June 21, 1982. Reply comments in response to comments filed in the initial comment period could be submitted by July 21, 1982.

In accordance with § 330.10(a)(10), the data and information considered by the Panel were put on public display in the Dockets Management Branch (HFA- 305), Food and Drug Administration (address above), after deletion of a small amount of trade secret information. In response to the advance notice of proposed rulemaking, eight drug manufacturers, one drug manufacturer association, one counsulting firm, three physicians, and one consumer submitted comments. Copies of the comments received are on public display in the Dockets Management Branch.

List of Subjects in 21 CFR Part 333

OTC drugs; Topical acne drug products.

Therefore, under the Federal Food, Drug, and Cosmetic Act (secs. 201(p), 502, 505, 701, 52 Stat. 1041-1042 as amended, 1050-1053 as amended, 1055-1056 as amended by 70 Stat. 919 and 72 Stat. 948 (21 U.S.C. 321(p), 352, 355, 371)) and the Administrative Procedure Act (secs. 4, 5, and 10, 60 Stat. 238 and 243 as amended (5 U.S.C. 553, 554, 702, 703, 704)) and under 21 CFR 5.11, it is proposed that Subchapter D of Chapter I of Title 21 of the Code of Federal Regulations be amended in Part 333 (which was proposed to be added in the Federal Register of January 6, 1978 (42 FR 1210)) by revising proposed Subpart D, to read as follows:

PART 333--TOPICAL ANTIMICROBIAL DRUG PRODUCTS FOR OVER-THE-COUNTER HUMAN USE

Subpart D--Topical Acne Drug Products

Authority: Secs. 201(p), 502, 505, 701, 52 Stat. 1041-1042 as amended, 1050- 1053 as amended, 1055-1056 as amended by 70 Stat. 919 and 72 Stat. 948 (21 U.S.C. 321(p), 352, 355, 371); secs. 4, 5, and 10, 60 Stat. 238 and 243 as amended (5 U.S.C. 553, 554, 702, 703, 704).

Subpart D--Topical Acne Drug Products

§ 333.301 Scope.

(a) An over-the-counter acne drug product in a form suitable for topical administration is generally recognized as safe and effective and is not misbranded if it meets each of the conditions in this subpart and each general condition established in § 330.1.

(b) References in this subpart to regulatory sections of the Code of Federal Regulations are to Chapter I of Title 21 unless otherwise noted.

§ 333.303 Definitions.

As used in this subpart:

(a) Acne. An inflammatory skin disease involving the oil glands and hair follicles of the skin.

(b) Acne drug product. A drug product used to reduce the number of acne lesions.

(c) Blackhead. An acne lesion characterized by a black tip.

(d) Pimple. A small, prominent, inflamed elevation of the skin.

§ 333.310 Acne active ingredients.

The active ingredient of the product consists of any of the following when labeled according to § 333.350.

(a) Benzoyl peroxide 2.5 to 10 percent.

(b) Resorcinol 2 percent when combined in accordance with § 333.320(a).

(c) Resorcinol monoacetate 3 percent when combined in accordance with § 333.320(b)

(d) Salicylic acid 0.5 to 2 percent.

(e) Sulfur 3 to 10 percent.

(f) Sulfur 3 to 8 percent when combined in accordance with § 333.320.

§ 333.320 Permitted combinations of active ingredients.

(a) Resorcinol identified in § 333.310(b) when combined with sulfur identified in § 333.310(f) provided the product is labeled according to § 333.350.

(b) Resorcinol monoacetate identified in § 333.310(c) when combined with sulfur identified in § 333.310(f) provided the product is labeled according to § 333.350.

§ 333.350 Labeling of acne drug products.

(a) Statement of identity. The labeling of the product contains the established name of the drug, if any, and identifies the product as an "acne medication."

(b) Indications. The labeling of the product contains a statement of the indications under the heading "Indications" that is limited to the following:

(1) "For the" (select one of the following: "treatment" or "management") "of acne."

(2) Other allowable indications. In addition to the required indication identified in paragraph (b)(1) of this section, the labeling of the product may contain additional indication statements that are limited to one or more of the following:

(i) (Select one of the following: "Dries," "Dries up," "Dries and clears," "Clears," "Clears up," "Clears up most," "Helps clear," "Helps clear up," "Reduces the number of," or "Reduces the severity of") (select one or more of the following: "blackheads," "acne pimples," or "acne blemishes") which may be followed by "and allows skin to heal."

(ii) "Penetrates pores to" (select one of the following: "eliminate most," "control," "clear most," or "reduce the number of") (select one or both of the following: "blackheads" or "acne pimples").

(iii) "Helps keep skin clear and new acne pimples."

(iv) "Helps prevent new" (select one or more of the following: "blackheads," "acne pimples," or "acne blemishes") which may be followed by "from forming."

(v) "Helps prevent the development of new acne pimples."

(c) Warnings. The labeling of the product contains the following warnings under the heading "Warnings":

(1) For products containing any ingredient identified in § 333.310. (i) "For external use

EXHIBIT C

United States Patent **5,314,747**
Malhotra , et al. **May 24, 1994**

Recording sheets containing cationic sulfur compounds

Abstract

Disclosed is a recording sheet which comprises (a) a base sheet; (b) a cationic sulfur compound selected from the group consisting of sulfonium compounds, thiazolium compounds, benzothiazolium compounds, and mixtures thereof; (c) an optional binder; and (d) an optional pigment.

Inventors: **Malhotra; Shadi L.** (Mississauga, CA); **Bryant; Brent S.** (Milton, CA)
Assignee: **Xerox Corporation** (Stamford, CT)
Appl. No.: **034943**
Filed: **March 19, 1993**

Current U.S. Class: **428/341**; 347/105; 427/256; 427/288; 428/195; 428/211; 428/342; 428/704
Intern'l Class: B41M 005/00
Field of Search: 346/1.1,135.1 427/256,288 428/195,211,341,342,704

References Cited [Referenced By]

U.S. Patent Documents

4446174	May., 1984	Maekawa et al.	427/261.
4554181	Nov., 1985	Cousin et al.	427/261.
4576867	Mar., 1986	Miyamoto	428/342.
4740420	Apr., 1988	Akutsu et al.	428/341.
4830911	May., 1989	Kojima et al.	428/342.
4877680	Oct., 1989	Sakaki et al.	428/332.

Foreign Patent Documents

0439363	Jul., 1991	EP	428/195.

Primary Examiner: Schwartz; Pamela R.
Attorney, Agent or Firm: Byorick; Judith L.

Claims

What is claimed is:

1. An imaged recording sheet which comprises (a) a substrate; and (b) a recording layer comprising a ***cationic sulfur compound*** selected from the group consisting of sulfonium compounds, thiazolium compounds, benzothiazolium compounds, and mixtures thereof, an optional binder, and an optional pigment, said recording layer containing an image applied from an aqueous ink.

2. A recording sheet according to claim 1 wherein the substrate is paper.

3. A recording sheet according to claim 1 wherein the substrate is transparent.

4. A recording sheet according to claim 1 wherein the cationic sulfur compound is selected from the group consisting of ##STR30## wherein R.sub.1, R.sub.2, R.sub.3, R.sub.4, and R.sub.5 are independently selected from the group consisting of hydrogen, alkyl groups, substituted alkyl groups, aryl groups, substituted aryl groups, arylalkyl groups, substituted arylalkyl groups, and amine groups, and wherein X is an anion.

5. A recording sheet according to claim 4 wherein R.sub.1, R.sub.2, R.sub.3, R.sub.4, and R.sub.5 are independently selected from the group consisting of alkyl groups with from 1 to about 35 carbon atoms, substituted alkyl groups with from 1 to about 35 carbon atoms, aryl groups with from 1 to about 25 carbon atoms, substituted aryl groups with from 1 to about 25 carbon atoms, arylalkyl groups with from 7 to about 25 carbon atoms, and substituted arylalkyl groups with from 7to about25carbon atoms.

6. A recording sheet according to claim 4 wherein the substituents on R.sub.1, R.sub.2, R.sub.3, R.sub.4, and R.sub.5 are independently selected from the group consisting of silyl groups, halide atoms, nitro groups, amine groups, hydroxy groups, ether groups, aldehyde groups, ketone groups, ester groups, amide groups, carboxylic acid groups, and mixtures thereof.

7. A recording sheet according to claim 1 wherein the cationic sulfur compound is selected from the group consisting of trimethyl sulfonium methyl sulfate, trimethyl sulfonium iodide, trimethyl sulfoxonium iodide, trimethyl sulfoxonium chloride, triphenyl methane sulfenyl chloride, (2-chloroethyl) dimethyl sulfonium iodide, dimethyl (2-methoxy-5-nitrobenzyl) sulfonium bromide, thionin perchlorate, p-xylylene bis(tetrahydrothiopheneum chloride), tris (dimethyl amino) sulfonium difluorotrimethyl silicate, tris (dimethyl amino) sulfonium trifluoromethoxide, (3-amino-3-carboxypropyl) dimethyl sulfonium chloride, 3-ethyl-2-methyl-2-thiazollum iodide, 3,4-dlmethyl-5-(2-hydroxyethyl) thiazollum iodide, 3-ethyl-5-(2-hydroxyethyl)-4-methyl thiazollum bromide, 3-benzyl-5-(2-hydroxyethyl)-4-methyl thiazolium chloride, thiamine hydrochloride, 3-(carboxymethyl) benzothiazolium bromide, 2-azido-3-ethyl benzothiazollum tetrafluoroborate, 3-ethyl-2-methyl benzothiazolium iodide, 2-methyl-3-propyl benzothiazolium iodide, 3-ethyl-2-(2-hydroxy-1-propenyl) benzothiazolium chloride, 3,6-dimethyl-2-(4-dimethyl aminophenyl) benzothiazolium bromide, and mixtures thereof.

8. A recording sheet according to claim 1 wherein the cationic sulfur compound is present in an amount of from about 1 to about 25 percent by weight of the substrate.

9. A recording sheet according to claim 1 wherein the cationic sulfur compound is present in an amount of from about 5 to about 15 percent by weight of the substrate.

10. A recording sheet according to claim 1 wherein the cationic sulfur compound is present in an amount of from about 0.3 to about 7.5 grams per square meter of the substrate surface to which it is applied.

11. A process which comprises applying an aqueous recording liquid to a recording sheet in an imagewise pattern, said recording sheet comprising (a) a substrate; and (b) a recording layer comprising a cationic sulfur compound selected from the group consisting of sulfonium compounds, thiazolium compounds, benzothiazolium compounds, and mixtures thereof, an optional binder, and an optional pigment.

12. A printing process which comprises (1) incorporating into an ink jet printing apparatus containing an aqueous ink a recording sheet comprising (a) a substrate; and (b) a recording layer comprising a cationic sulfur compound selected from the group consisting of sulfonium compounds, thiazolium compounds, benzothiazolium compounds, and mixtures thereof, an optional binder, and an optional pigment, and (2) causing droplets of the ink to be ejected in an imagewise pattern onto the recording sheet, thereby generating images on the recording sheet.

13. A printing process according to claim 12 wherein the substrate is paper.

14. A printing process according to claim 12 wherein the substrate is transparent.

15. A printing process according to claim 12 wherein the cationic sulfur compound is selected from the group consisting of ##STR31## wherein R.sub.1, R.sub.2, R.sub.3, R.sub.4, and R.sub.5 are independently selected from the group consisting of hydrogen, alkyl groups, substituted alkyl groups, aryl groups, substituted aryl groups, arylalkyl groups, substituted arylalkyl groups, and amine groups, and wherein X is an anion.

16. A printing process according to claim 15 wherein R.sub.1, R.sub.2, R.sub.3, R.sub.4, and R.sub.5 are independently selected from the group consisting of alkyl groups with from 1 to about 35 carbon atoms, substituted alkyl groups with from 1 to about 35 carbon atoms, aryl groups with from 1 to about 25 carbon atoms, substituted aryl groups with from 1 to about 25 carbon atoms, arylalkyl groups with from 7 to about 25 carbon atoms, and substituted arylalkyl groups with from 7 to about 25 carbon atoms.

17. A printing process according to claim 15 wherein the substituents on R.sub.1, R.sub.2, R.sub.3, R.sub.4, and R.sub.5 are independently selected from the group consisting of silyl groups, halide atoms, nitro groups, amine groups, hydroxy groups, ether groups, aldehyde groups, ketone groups, ester groups, amide groups, carboxylic acid groups, and mixtures thereof.

18. A printing process according to claim 12 wherein the cationic sulfur compound is selected from the group consisting of trimethyl sulfonium methyl sulfate, trimethyl sulfonium iodide, trimethyl sulfoxonium iodide, trimethyl sulfoxonium chloride, triphenyl methane sulfenyl chloride, (2-chloroethyl) dimethyl sulfonium iodide, dimethyl (2-methoxy-5-nitrobenzyl) sulfonium bromide, thionin perchlorate, p-xylylene bis(tetrahydrothlopheneum chloride), tris (dimethyl amino) sulfonium difluorotrimethyl silicate, tris (dimethyl amino) sulfonium trifluoromethoxide, (3-amino-3-carboxypropyl) dimethyl sulfonium chloride, 3-ethyl-2-methyl-2-thiazollum iodide, 3,4-dimethyl-5-(2-hydroxyethyl) thiazolium iodide, 3-ethyl-5-(2-hydroxyethyl)-4-methyl thiazolium bromide, 3-benzyl-5-(2-hydroxyethyl)-4-methyl thiazolium chloride, thiamine hydrochloride, 3-(carboxymethyl)

benzothiazolium bromide, 2-azido-3-ethyl benzothiazolium tetrafluoroborate, 3-ethyl-2-methyl benzothiazolium iodide, 2-methyl-3-propyl benzothiazolium iodide, 3-ethyl-2-(2-hydroxy-1-propenyl) benzothiazolium chloride, 3,6-dimethyl-2-(4-dimethyl aminophenyl) benzothiazolium bromide, and mixtures thereof.

19. A printing process according to claim 12 wherein the cationic sulfur compound is present in an amount of from about 1 to about 25 percent by weight of the substrate.

20. A printing process according to claim 12 wherein the cationic sulfur compound is present in an amount of from about 5 to about 15 percent by weight of the substrate.

21. A printing process according to claim 12 wherein the cationic sulfur compound is present in an amount of from about 0.3 to about 7.5 grams per square meter of the substrate surface to which it is applied.

22. A printing process according to claim 12 wherein the printing apparatus employs a thermal ink jet process wherein the ink in the nozzles is selectively heated in an imagewise pattern, thereby causing droplets of the ink to be ejected in imagewise pattern.

Description

BACKGROUND OF THE INVENTION

The present invention is directed to recording sheets, such as transparently materials, filled plastics, papers, and the like. More specifically, the present invention is directed to recording sheets particularly suitable for use in ink jet printing processes. One embodiment of the present invention is directed to a recording sheet which comprises (a) a base sheet; (b) a cationic sulfur compound selected from the group consisting of sulfonium compounds, thiazolium compounds, benzothiazolium compounds, and mixtures thereof; (c) an optional binder; and (d) an optional pigment.

Recording sheets suitable for use in ink jet printing are known. For example, U.S. Pat. No. 4,740,420 (Akutsu et al.) discloses a recording medium for ink jet printing comprising a support material containing at least in the surface portion thereof a water soluble metal salt with the ion valence of the metal thereof being 2 to 4 and a cationic organic material. The cationic organic materials include salts of alkylamines, quaternary ammonium salts, polyamines, and basic latexes.

U.S. Pat. No. 4,576,867 (Miyamoto) discloses an ink jet recording paper with improved water resistance and sunlight fastness of the image formed on the paper wherein the recording paper has attached to its surface a cationic resin of the formula ##STR1## wherein R.sub.1, R.sub.2, and R.sub.3 represent alkyl groups, m represents a number of 1 to 7, and n represents a number of 2 to 20, and Y represents an acid residue.

U.S. Pat. No. 4,446,174 (Maekawa et al.) discloses an ink jet recording method for producing a recorded image on an image receiving sheet with a jet of aqueous ink, wherein an ink jet is projected onto an image receiving sheet comprising a surface layer containing a pigment, and wherein the surface layer is capable of absorbing a coloring component in the aqueous ink. Poly (vinyl benzyl trimethyl ammonium chloride), poly (diallyl dimethyl ammonium chloride), and poly (methacryloxyethyl-.beta.-hydroxyethyl dimethyl ammonium chloride) are disclosed as dye absorbing adhesive materials.

U.S. Pat. No. 4,830,911 (Kojima et al.) discloses a recording sheet for ink jet printers which gives an image by the use of an aqueous ink containing a water-soluble dye, coated or impregnated with either of or a mixture of two kinds of water soluble polymers, one whose polymeric unit is alkylquaternaryammonium (meth)acrylate and the other whose polymer unit is alkylquaternaryammonium (meth)acrylamide, wherein the water soluble polymers contain not less than 50 mol percent of a monomer represented by the formula ##STR2## where R represents hydrogen or methyl group, n is an interger from 1 to 3 inclusive, R.sub.1, R.sub.2, and R.sub.3 represent hydrogen or the same or different aliphatic alkyl group with 1 to 4 carbon atoms, X represents an anion such as a halogen ion, sulfate ion, alkyl sulfate ion, alkyl sulfonate ion, aryl sulfonate ion, and acetate ion, and Y represents oxygen or imino group.

U.S. Pat. No. 4,554,181 (Cousin et al.) discloses an ink jet recording sheet having a recording surface which includes a combination of a water soluble polyvalent metal salt and a cationic polymer, the polymer having cationic groups which are available in the recording surface for insolubilizing an anionic dye.

U.S. Pat. No. 4,877,680 (Sakaki et al.) discloses a recording medium comprising a substrate and a nonporous ink receiving layer. The ink receiving layer contains a water-insoluble polymer containing a cationic resin. The recording medium may be employed for recording by attaching droplets of a recording liquid thereon.

European Patent Publication 0 439 363 A1, published Jul. 31, 1991, corresponding to copending application U.S. Ser. No. 07/469,985, filed Jan. 25, 1990, the disclosure of which is totally incorporated herein by reference, discloses a paper which comprises a supporting substrate with a coating comprising (a) a desizing component selected from the group consisting of (1) hydrophilic poly(dialkylsiloxanes); (2) poly(alkylene glycol); (3) poly(propylene oxide) - poly(ethylene oxide) copolymers; (4) fatty ester modified compounds of phosphate, sorbitan, glycerol, poly(ethylene glycol), sulfosuccinic acid, sulfonic acid and alkyl amine; (5) poly(oxyalkylene) modified compounds of sorbitan esters, fatty amines, alkanol amides, castor oil, fatty acids and fatty alcohols; (6) quaternary alkosulfate compounds; (7) fatty imidazolines; and mixtures thereof, and (b) a hydrophilic binder polymer. The binder polymer may be a quaternary ammonium copolymer such as Mirapol WT, Mirapol AD-1, Mirapol AZ-1, Mirapol A-15, Mirapol-9, Merquat-100, or Merquat-550, available from Miranol Incorporated.

U.S. Pat. No. 5,223,338, the disclosure of which is totally incorporated herein by reference, discloses a recording sheet which comprises a substrate and a coating consisting essentially of (1) quaternary ammonium polymers selected from the group consisting of (a) polymers of Formula I ##STR3## wherein n is an integer of from 1 to about 200, R.sub.1, R.sub.2, R.sub.3, and R.sub.4 are each independently selected from the group consisting of alkyl groups, hydroxyalkyl groups, and polyoxyalkylene groups, p Is an integer of from 1 to about 10, q is an integer of from 1 to about 10, X is an anion, and Y.sub.1 is selected from the group consisting of --CH.sub.2 CH.sub.2 OCH.sub.2 CH.sub.2 --, --CH.sub.2 CH.sub.2 OCH.sub.2 OCH.sub.2 CH.sub.2 --, --(CH.sub.2).sub.k --, wherein k is an integer of from about 2 to about 10, and --CH.sub.2 CH(OH)CH.sub.2 --; (b) polymers of Formula II ##STR4## wherein n is an integer of from 1 to about 200, R.sub.5, R.sub.6, R.sub.7, and R.sub.8 are each independently selected from the group consisting of alkyl groups, hydroxyalkyl groups, and polyoxyalkylene groups, m is an integer of from 0 to about 40, r Is an integer of from 1 to about 10, s is an integer of from 1 to about 10, X is an anion, and Y.sub.2 is selected from the group consisting of --CH.sub.2 CH.sub.2 OCH.sub.2 CH.sub.2 --, --CH.sub.2 CH.sub.2 OCH.sub.2 CH.sub.2 OCH.sub.2 CH.sub.2 --, --(CH.sub.2).sub.k --, wherein k is an integer of from about 2 to about 10, and --CH.sub.2 CH(OH)CH.sub.2 --; (c) copolymers of Formula III ##STR5## wherein a and b are each integers wherein the sum of a+b is from about 2 to about 200, R.sub.1, R.sub.2, R.sub.3, R.sub.4, R.sub.5, R.sub.6, R.sub.7, and R.sub.8 are each independently selected from the group consisting of alkyl groups,

hydroxyalkyl groups, and polyoxyalkylene groups, p Is an integer of from 1 to about 10, q is an integer of from 1 to about 10, X is an anion, and Y.sub.1 and Y.sub.2 are each independently selected from the group consisting of –CH.sub.2 CH.sub.2 OCH.sub.2 CH.sub.2 --, –CH.sub.2 CH.sub.2 OCH.sub.2 CH.sub.2 OCH.sub.2 CH.sub.2 --, --(CH.sub.2).sub.k --, wherein k is an integer of from about 2 to about 10, and --CH.sub.2 CH(OH)CH.sub.2 --; (d) mixtures of polymers of Formula I and polymers of Formula II; (e) mixtures of polymers of Formula I and copolymers of Formula III; (f) mixtures of polymers of Formula II and copolymers of Formula III; and (g) mixture of polymers of Formula I, polymers of Formula II, and copolymers of Formula III; (2) an optional binder polymer; and (3) an optional filler.

U.S. Pat. No. 5,212,008, the disclosure of which is totally incorporated herein by reference, discloses a recording sheet which comprises a substrate; a first coating in contact with the substrate which comprises a crosslinking agent selected from the group consisting of hexamethoxymethyl melamine, methylated melamine-formaldehyde, methylated urea-formaldehyde, cationic ureaformaldehyde, cationic polyamine-epichlorohydrin, glyoxal-urea resin, poly (aziridine), poly (acrylamide), poly (N,N-dimethyl acrylamide), acrylamide-acrylic acid copolymer, poly (2-acrylamido-2-methyl propane sulfonic acid), poly (N,N-dimethyl-3,5-dimethylene piperldinium chloride), poly (methylene-guanidine) hydrochloride, poly (ethylene imine) poly (ethylene imine) epichlorohydrin, poly (ethylene imine) ethoxylated, glutaraldehyde, and mixtures thereof; a catalyst; and a polymeric material capable of being crosslinked by the crosslinking agent and selected from the group consisting of polysaccharides having at least one hydroxy group, polysaccharides having at least one carboxy group, polysaccharides having at least one sulfate group, polysaccharides having at least one amine or amino group, polysaccharide gums, poly (alkylene oxides), vinyl polymers, and mixtures thereof; and a second coating in contact with the first coating which comprises a binder and a material selected from the group consisting of fatty imidazolines, ethosulfate quaternary compounds, dialkyl dimethyl methosulfate quaternary compounds, alkoxylated di-fatty quaternary compounds, amine oxides, amine ethoxylates, imidazoline quaternary compounds, alkyl benzyl dimethyl quaternary compounds, poly (eplamines), and mixtures thereof.

While known compositions and processes are suitable for their intended purposes, a ned remains for improved recording sheets. In addition, there is a need for improved recording sheets suitable for use in ink jet printing processes. Further, a need remains for recording sheets for ink jet printing with a high degree of water fastness. Additionally, there is a need for paper recording sheets for ink Jet printing with reduced show through of the images on the side of the paper opposite to that printed. There is also a need for recording sheets for ink jet printing with enhanced optical density.

SUMMARY OF THE INVENTION

It is an object of the present Invention to provide recording sheets with the above noted advantages.

It is another object of the present invention to provide recording sheets suitable for use in ink jet printing processes.

It is yet another object of the present Invention to provide recording sheets recording sheets for ink jet printing with a high degree of water fastness.

It is still another object of the present invention to provide paper recording sheets for ink jet printing with reduced show through of the images on the side of the paper opposite to that printed.

Another object of the present invention is to provide recording sheets for ink jet printing with enhanced optical density.

These and other objects of the present invention (or specific embodiments thereof) can be achieved by providing a recording sheet which comprises (a) a base sheet; (b) a cationic sulfur compound selected from the group consisting of sulfonium compounds, thiazolium compounds, benzothiazolium compounds, and mixtures thereof; (c) an optional binder; and (d) an optional pigment.

DETAILED DESCRIPTION OF THE INVENTION

The recording sheets of the present invention comprise a substrate and at least two coating layers on one or both surfaces of the substrate. Any suitable substrate can be employed. Examples include transparent materials, such as polyester, including Mylar.TM., available from E. I. Du Pont de Nemours & Company, Melinex.TM., available from Imperial Chemicals, Inc., Celanar.TM., available from Celanese Corporation, polycarbonates such as Lexan.TM., available from General Electric Company, polysulfones, such as those available from Union Carbide Corporation, polyether sulfones, such as those prepared from4,4'-diphenyl ether, such as Udel.TM., available from Union Carbide Corporation, those prepared from disulfonyl chloride, such as Victrex.TM., available from ICI America Incorporated, those prepared from biphenylene, such as Astrel.TM., available from 3M Company, poly (arylene sulfones), such as those prepared from crosslinked poly(arylene ether ketone sulfones), cellulose triacetate, polyvinylchloride cellophane, polyvinyl fluoride, polyamides, and the like, with polyester such as Mylar.TM. being preferred in view of its availability and relatively low cost. The substrate can also be opaque, including opaque plastics, such as Teslin.TM., available from PPG Industries, and filled polymers, such as Melinex.RTM., available from ICI. Filled plastics can also be employed as the substrate, particularly when it is desired to make a "never-tear paper" recording sheet. Paper is also suitable, including plain papers such as Xerox.RTM. 4024, diazo papers, or the like.

In one embodiment of the present invention, the substrate comprises sized blends of hardwood kraft and softwood kraft fibers containing from about 10 to 90 percent by weight soft wood and from about 10 to about 90percent by weight hardwood. Examples of hardwood include Seagull W dry bleached hardwood kraft, present in one embodiment in an amount of about 70 percent by weight. Examples of softwood Include La Tuque dry bleached softwood kraft, present in one embodiment in an amount of about 30percent by weight. These substrates can also contain fillers and pigments in any effective amounts, typically from about 1 to about 60 percent by weight, such as clay (available from Georgia Kaolin Company, Astro-fil 90 clay, Engelhard Ansilex clay), titanium dioxide (available from Tioxide Company - Anatase grade AHR), calcium silicate CH-427-97 P-974 (J. M. Huber Corporation), and the like. The sized substrates can also contain sizing chemicals In any effective amount, typically from about 0.25 percent to about 25 percent by weight of pulp, such as acidic sizing, including Mon size (available from Monsanto Company), alkaline sizing such as Hercon-76 (available from Hercules Company), Alum (available from Allied Chemicals as Iron free alum), retention aid (available from Allied Colioids as Percol 292), and the like. The preferred internal sizing degree of papers selected for the present invention, including commercial Iyaval lable papers, varies from about 0.4 to about 5,000 seconds, and papers in the sizing range of from about 0.4 to about 300 seconds are more preferred, primarily to decrease costs. Preferably, the selected substrate is porous, and the porosity value of the selected substrate preferably varies from about 100 to about 1,260 milliliters per minute and preferably from about 50 to about 600 milliliters per minute to enhance the effectiveness of the recording sheet in ink jet processes. Preferred basis weights for the substrate are from about 40 to about 400 grams per square meter, although the basis weight can be outside of this range.

Illustrative examples of commercially available internally and externally (surface) sized substrates suitable for the present invention include Diazo papers, offset papers, such as Great Lakes offset, recycled papers, such as conservatree, office papers, such as automimeo, Eddy liquid toner paper and copy papers available from companies such as Nekoosa, Champion, Wiggins Teape, Kymmene, Modo, Domtar, Veitsiluoto and Sanyo, and the like, with Xerox.RTM.4024.TM. papers and sized calcium

silicateclay filled papers being particularly preferred in view of their availability, reliability, and low print through. Pigmented filled plastics, such as Teslin (available from PPG industries), are also preferred as supporting substrates.

The substrate can be of any effective thickness. Typical thicknesses for the substrate are from about 50 to about 500 microns, and preferably from about 100 to about 125 microns, although the thickness can be outside these ranges.

Situated on the substrate of the present invention is one or more cationic sulfur compounds, wherein the compound contains either a positively charged ionic sulfur atom or a sulfur atom covalently bonded to another atom wherein the sulfur atom tends to be partially positively charged and the other atom tends to be partially negatively charged. One class of suitable cationic sulfur compounds is that of sulfonium compounds, of the general formulae ##STR6## wherein R.sub.1, R.sub.2, R.sub.3, R.sub.4, and R.sub.5 are independently selected from the group consisting of hydrogen, alkyl groups, preferably with from 1 to about 35 carbon atoms, more preferably with from 1 to about 25 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, hexyl, and the like, and including cyclic alkyl groups, such as cyclopropyl, cyclohexyl, and the like, and including unsaturated alkyl groups, such as vinyl (H.sub.2 C=CH–), allyl (H.sub.2 C=CH–CH.sub.2 --), propynyl (HC=--C--CH.sub.2 --), and the like, substituted alkyl groups, preferably with from 1 to about 35 carbon atoms, more preferably from 1 to about 25 carbon atoms, aryl groups, preferably with from 1 to about 25 carbon atoms, substituted aryl groups, preferably with from 1 to about 25 carbon atoms, arylalkyl groups, preferably with from 7 to about 25 carbon atoms, such as benzyl and the like, and substituted arylalkyl groups, preferably with from 7 to about 25 carbon atoms, and wherein X is an anion. Any two R groups attached to sulfur can also be joined to form a ring. Any suitable anion can be employed. Examples of suitable anions include halide anions, such as fluoride, chloride, bromide, iodide, and astatide, sulfate, alkosulfate, such as methylsulfate and ethylsulfate, sulfite, phosphate, phosphate, perhalate, such as perchlorate, perbromate, periodate, and the like, halate, such as chlorate and the like, halite, such as bromite and the like, fluoroborate, and the like. Examples of suitable substituents on the alkyl, aryl, and arylalkyl groups include silyl groups, halide atoms, such as fluoride, chloride, bromide, iodide, and astatide, nitro groups, amine groups, including primary, secondary, and tertiary amines, hydroxy groups, alkoxy or ether groups, aldehyde groups, ketone groups, ester groups, amide groups, carboxylic acid groups, and the like. Also suitable are compounds wherein R.sub.1, R.sub.2, and/or R.sub.3 are nitrogen atoms; for example, R.sub.1, R.sub.2, and R.sub.3 can each be dimethylamine groups bonded to sulfur.

Monosulfonium compounds containing one sulfonium ion group are suitable, as are disulfonium compounds containing two sulfonium ion groups and polysulfonium compounds containing more than two sulfonium ion groups. Examples of suitable sulfonium compounds include trimethyl sulfonium methyl sulfate (Aldrich Chemical Co. 30,359-3) and trimethyl sulfonium iodide (Aldrich T8-048-9), of the formulae ##STR7## trimethyl sulfoxonium iodide (Aldrich T8,050-0) and trimethyl sulfoxomium chloride (Aldrich 29,300-8), of the formulae ##STR8## triphenyl methane sulfenyl chloride (Aldrich 27,696-0), of the formula ##STR9## (2-chlorethyl)dimethyl sulfonium iodide (Aldrich 27,696), of the formula ##STR10## dimethyl (2-methoxy-5-nitrobenzyl) sulfonium bromide (Aldrich 85,775-0), of the formula ##STR11## thionin perchlorate (Aldrich 34,115-0), of the formula ##STR12## p-xylylene bis (tetrahydrothiopheneum chloride) (Aldrich 37,708-2), of the formula ##STR13## tris (dimethyl amino) sulfonium difluorotrimethyl silicate (Fluka 93336), of the structure ##STR14## tris (dimethyl amino) sulfonium trifluoromethoxide (Fluka 93343), of the formula ##STR15## (3-amino-3-carboxypropyl) dimethyl sulfonium chloride (Fluka 64382), of the formula ##STR16## and the like.

Another class of suitable cationic sulfur compounds is that of thiazolium compounds, of the general formula ##STR17## wherein R.sub.1 is a moiety bound to the nitrogen atom and is selected from the group consisting of hydrogen, alkyl groups, preferably with from 1 to about 25 carbon atoms, including

cyclic alkyl groups, such as cyclopropyl, cyclohexyl, and the like, and including unsaturated alkyl groups, such as vinyl (H.sub.2 C.dbd.CH--), allyl (H.sub.2 C.dbd.CH--CH.sub.2 --), propynyl (HC.tbd.C--CH.sub.2 --), and the like, substituted alkyl groups, preferably with from 1 to about 25 carbon atoms, aryl groups, preferably with from 6 to about 25 carbon atoms, substituted aryl groups, preferably with from 6 to about 25 carbon atoms, arylalkyl groups, preferably with from 7 to about 25 carbon atoms, such as benzyl and the like, substituted arylalkyl groups, preferably with from 7 to about 25 carbon atoms, R.sub.2 is a moiety bound to the ring at an atom other than nitrogen and is selected from the group consisting of hydrogen, alkyl groups, preferably with from 1 to about 25 carbon atoms, including cyclic alkyl groups, such as cyclopropyl, cyclohexyl, and the like, and including unsaturated alkyl groups, such as vinyl (H.sub.2 C=CH--), allyl (H.sub.2 C=CH--CH.sub.2 --), propynyl (HC=C--CH.sub.2 --), and the like, substituted alkyl groups, preferably with from 1 to about 25 carbon atoms, aryl groups, preferably with from 6 to about 25 carbon atoms, substituted aryl groups, preferably with from 6 to about 25 carbon atoms, arylalkyl groups, preferably with from 7 to about 25 carbon atoms, such as benzyl and the like, substituted arylalkyl groups, preferably with from 7 to about 25 carbon atoms, n represents the number of R.sub.2 substituents on the ring, and X is an anion. Examples of suitable substituents on R.sub.1 and R.sub.2 include silyl groups, halide atoms, such as fluoride, chloride, bromide, iodide, and astatide, nitro groups, amine groups, including primary, secondary, and tertiary amines, hydroxy groups, alkoxy or ether groups, aldehyde groups, ketone groups, ester groups, amide groups, carboxylic acid groups, and the like. Any suitable anion can be employed. Examples of suitable anions include halide anions, such as fluoride, chloride, bromide, iodide, and astatide, sulfate, alkosulfate, such as methylsulfate and ethylsulfate, sulfite, phosphate, phosphite, perhalate, such as perchlorate, perbromate, periodate, and the like, halate, such as chlorate and the like, halite, such as bromite and the like, fluoroborate, and the like.

Examples of suitable thiazollum salts include 3-ethyl-2-methyl-2thiazolium iodide (Aldrich 32,249-0), of the formula ##STR18## 3,4-dimethyl-5-(2-hydroxyethyl) thiazolium iodide, of the formula ##STR19## 3-ethyl-5-(2-hydroxyethyl)-4-methyl thiazolium bromide (Aldrich 33,124-4), of the formula ##STR20## 3-benzyl-5-(2-hydroxyethyl)-4-methyl thiazolium chloride (Aldrich 25,623-4), of the formula ##STR21## thiamine hydrochloride (Aldrich 10,917-7), of the formula ##STR22## and the like.

Another class of suitable cationic sulfur compounds is that of benzothiazolium compounds, of the general formula ##STR23## wherein R.sub.1 is a moiety bound to the nitrogen atom and is selected from the group consisting of hydrogen, alkyl groups, preferably with from 1 to about 25 carbon atoms, including cyclic alkyl groups, such as cyclopropyl, cyclohexyl, and the like, and including unsaturated alkyl groups, such as vinyl (H.sub.2 C.dbd.CH--), allyl (H.sub.2 C.dbd.CH--CH.sub.2 --), propynyl (HC.tbd.C--CH.sub.2 --), and the like, substituted alkyl groups, preferably with from 1 to about 25 carbon atoms, aryl groups, preferably with from 6 to about 25 carbon atoms, substituted aryl groups, preferably with from 6 to about 25 carbon atoms, arylalkyl groups, preferably with from 7 to about 15 carbon atoms, such as benzyl and the like, substituted arylalkyl groups, preferably with from 7 to about 15 carbon atoms, R.sub.2 is a moiety bound to either of the rings at an atom other than nitrogen and is selected from the group consisting of hydrogen, alkyl groups, preferably with from 1 to about 25 carbon atoms, including cyclic alkyl groups, such as cyclopropyl, cyclohexyl, and the like, and including unsaturated alkyl groups, such as vinyl (H.sub.2 C.dbd.CH--), allyl (H.sub.2 C.dbd.CH--CH.sub.2 --), propynyl (HC.dbd.C--CH.sub.2 --), and the like, substituted alkyl groups, preferably with from 1 to about 25 carbon atoms, aryl groups, preferably with from 6 to about 25 carbon atoms, substituted aryl groups, preferably with from 6 to about 25 carbon atoms, arylalkyl groups, preferably with from 7 to about 15 carbon atoms, such as benzyl and the like, substituted arylalkyl groups, preferably with from 7 to about 15 carbon atoms, represents the number of R.sub.2 substituents on the ring, and X is an anion. Examples of suitable substituents on R.sub.1 and R.sub.2 include silyl groups, halide atoms, such as fluoride, chloride, bromide, iodide, and astatide, nitro groups, amine groups, including primary,

secondary, and tertiary amines, hydroxy groups, alkoxy or ether groups, aldehyde groups, ketone groups, ester groups, amide groups, carboxylic acid groups, and the like. Any suitable anion can be employed. Examples of suitable anions include halide anions, such as fluoride, chloride, bromide, iodide, and astatide, sulfate, alkosulfate, such as methylsulfate and ethylsulfate, sulfite, phosphate, phospite, perhalate, such as perchlorate, perbromate, periodate, and the like, halate, such as chlorate and the like, halite, such as bromite and the like, fluoroborate, and the like. Any two R.sub.2 groups can also be joined together to form one or more additional rings.

Examples of suitable benzothiazolium salts include 3-(carboxymethyl) benzothiazolium bromide (Aldrich 37,163-7), of the formula ##STR24## 2-azido-3-ethyl benzothiazolium tetrafluoroborate (Aldrich 36,065-1), of the formula ##STR25## 3-ethyl-2-methyl benzothiazolium iodide (Aldrich 37,700-7), of the formula ##STR26## 2-methyl-3-propyl benzothiazolium iodide (Aldrich 36,329-4), of the formula ##STR27## 3-ethyl-2-(2-hydroxy-l-propenyl) benzothiazolium chloride (Aldrich 29,365-2), of the formula ##STR28## 3,6-dimethyl-2-(4-dimethyl aminophenyl) benzothiazolium bromide (Aldrich 15,242-0), of the formula ##STR29## and the like.

Mixtures of any two or more cationic sulfur compounds can also be employed.

The cationic sulfur compound is present in any effective amount relative to the substrate. Typically, the cationic sulfur compound is present in an amount of from about 1 to about 25 percent by weight of the substrate, preferably from about 2 to about 10 percent by weight of the substrate, although the amount can be outside this range. The amount can also be expressed in terms of the weight of cationic sulfur compound per unit area of substrate. Typically, the cationic sulfur compound is present in an amount of from about 1 to about 10 grams per square meter of the substrate surface to which it is applied, and preferably from about 1 to about 5 grams per square meter of the substrate surface to which it is applied, although the amount can be outside these ranges. Higher concentrations of cationic sulfur compound are preferred for the purpose of enhancing the color of images printed on the recording sheets; the lower concentrations are adequate for enhancing the waterfastness of images printed on the recording sheets.

When the cationicsulfurcompound is applied to the substrate as a coating, the coatings employed for the recording sheets of the present invention can include an optional binder in addition to the cationic sulfur compound. Examples of suitable binder polymers include (a) hydrophilic polysaccharides and their modifications, such as (1) starch (such as starch SLS-280, available from St. Lawrence starch), (2) cationic starch (such as Cato-72, available from National Starch), (3) hydroxyalkylstarch, wherein alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from about 1 to about 20 carbon atoms, and more preferably from about 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl, or the like (such as hydroxypropyl starch (#02382, available from Poly Sciences Inc.) and hydroxyethyl starch (#06733, available from Poly Sciences Inc.)), (4) gelatin (such as Calfskin gelatin #00639, available from Poly Sciences Inc.), (5) alkyl celluloses and aryl celluloses, wherein alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, and even more preferably from 1 to about 7 carbon atoms, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, and the like (such as methyl cellulose (Methocel AM 4, available from Dow Chemical Company)), and wherein aryl has at least 6 carbon atoms and wherein the number of carbon atoms is such that the material is water soluble, preferably from 6to about 20 carbon atoms, more preferably from 6 to about 10 carbon atoms, and even more preferably about 6 carbon atoms, such as phenyl, (6) hydroxy alkyl celluloses, wherein alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, or the like (such as hydroxyethyl cellulose (Natrosol 250 LR, available from Hercules Chemical Company), and hydroxypropyl cellulose (Klucel Type E,

available from Hercules Chemical Company)), (7) alkyl hydroxy alkyl celluloses, wherein each alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, or the like (such as ethyl hydroxyethyl cellulose (Bermocoll, available from Berol Kem. A.B. Sweden)), (8) hydroxy alkyl alkyl celluloses, wherein each alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl and the like (such as hydroxyethyl methyl cellulose (HEM, available from British Celanese Ltd., also available as Tylose MH, MHK from Kalle A.G.), hydroxypropyl methyl cellulose (Methocel K35LV, available from Dow Chemical Company), and hydroxy butylmethyl cellulose (such as HBMC, available from Dow Chemical Company)), (9) dihydroxyalkyl cellulose, wherein alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material Is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl and the like (such as dihydroxypropyl cellulose, which can be prepared by the reaction of 3-chloro-1,2-propane with alkali cellulose), (10) hydroxy alkyl hydroxy alkyl cellulose, wherein each alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl and the like (such as hydroxypropyl hydroxyethyl cellulose, available from Aqualon Company), (11) halodeoxycellulose, wherein halo represents a halogen atom (such as chlorodeoxycellulose, which can be prepared by the reaction of cellulose with sulfuryl chloride in pyridine at 25.degree. C.), (12) amino deoxycellulose (which can be prepared by the reaction of chlorodeoxy cellulose with 19 percent alcoholic solution of ammonia for 6 hours at 160.degree. C.), (13) dialkylammonium halide hydroxy alkyl cellulose, wherein each alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl and the like, and wherein halide represents a halogen atom (such as diethylammonium chloride hydroxy ethyl cellulose, available as Celquat H-100, L-200, National Starch and Chemical Company), (14) hydroxyalkyl trialkyl ammonium halide hydroxyalkyl cellulose, wherein each alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl and the like, and wherein halide represents a halogen atom (such as hydroxypropyl trimethyl ammonium chloride hydroxyethyl cellulose, available from Union Carbide Company as Polymer JR), (15) dialkyl amino alkyl cellulose, wherein each alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl and the like, (such as diethyl amino ethyl cellulose, available from Poly Sciences Inc. as DEAE cellulose #05178), (16) carboxyalkyl dextrans, wherein alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, and the like, (such as carboxymethyl dextrans, available from Poly Sciences Inc. as # 16058), (17) dialkyl aminoalkyl dextran, wherein each alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl and the like (such as diethyl aminoethyl dextran, available from Poly Sciences Inc. as #5178), (18) amino dextran (available from Molecular Probes Inc), (19) carboxy alkyl cellulose salts, wherein alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl and the like, and wherein the cation is any conventional cation, such as sodium, lithium, potassium, calcium, magnesium, or the like (such as sodium carboxymethyl cellulose CMC 7HOF, available from Hercules Chemical Company), (20) gum arabic (such as #G9752, available from Sigma

Chemical Company), (21) carrageenan (such as #C1013 available from Sigma Chemical Company), (22) Karaya gum (such as #G0503, available from Sigma Chemical Company), (23) xanthan (such as Keltrol-T, available from Kelco division of Merck and Company), (24) chitosan (such as #C3646, available from Sigma Chemical Company), (25) carboxyalkyl hydroxyalkyl guar, wherein each alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl and the like (such as carboxymethyl hydroxypropyl guar, available from Auqualon Company), (26) cationic guar (such as Celanese Jaguars C-14-S, C-15, C-17, available from Celanese Chemical Company), (27) n-carboxyalkyl chitin, wherein alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl and the like, such as n-carboxymethyl chitin, (28) dialkyl ammonium hydrolyzed collagen protein, wherein alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl and the like (such as dimethyl ammonium hydrolyzed collagen protein, available from Croda as Croquats), (29) agaragar (such as that available from Pfaltz and Bauer Inc.), (30) cellulose sulfate salts, wherein the cation is any conventional cation, such assodium, lithium, potassium, calcium, magnesium, or the like (such assodium cellulose sulfate #023 available from Scientific Polymer Products), and (31) carboxyalkylhydroxyalkyl cellulose salts, wherein each alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl and the like, and wherein the cation is any conventional cation, such as sodium, lithium, potassium, calcium, magnesium, or the like (such as sodium carboxymethylhydroxyethyl cellulose CMHEC 43H and 37L available from Hercules Chemical Company); (b) vinyl polymers, such as (1) poly(vinyl alcohol) (such as Elvanol available from Dupont Chemical Company), (2) poly (vinyl phosphate) (such as #4391 available from Poly Sciences Inc.), (3) poly (vinyl pyrrolidone) (such as that available from GAF Corporation), (4) vinyl pyrrolidone-vinyl acetate copolymers (such as #02587, available from Poly Sciences Inc.), (5) vinyl pyrrolidone-styrene copolymers (such as #371, available from Scientific Polymer Products), (6) poly(vinylamine) (such as #1562,available from Poly Sciences Inc.), (7) poly (vinyl alcohol) alkoxylated, wherein alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl, and the like (such as poly (vinyl alcohol) ethoxylated #6573, available from Poly Sciences Inc.), and (8) poly (vinyl pyrrolidone-dialkylaminoalkyl alkylacrylate), wherein each alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl, and the like (such as poly (vinyl pyrrolidone-diethylaminomethylmethacrylate) #16294 and #16295, available from Poly Sciences Inc.); (c) formaldehyde resins, such as (1) melamine-formaldehyde resin (such as BC 309, available from British Industrial Plastics Limited), (2) urea-formaldehyde resin (such as BC777, available from British Industrial Plastics Limited), and (3) alkylated urea-formaldehyde resins, wherein alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl, and the like (such as methylated urea-formaldehyde resins, available from American Cyanamid Company as Beetle 65); (d) ionic polymers, such as (1) poly (2-acrylamide-2-methyl propane sulfonic acid) (such as #175 available from Scientific Polymer Products), (2) poly (N,N-dimethyl-3,5-dimethylene piperidinium chloride) (such as #401, available from Scientific Polymer Products), and (3) poly (methylene-guanidine) hydrochloride (such as #654, available from Scientific Polymer Products); (e) latex polymers, such as (1) cationic, anionic, and nonionic styrene-butadiene latexes (such as that available from Gen Corp Polymer Products, such as RES 4040 and RES 4100, available from Unocal Chemicals, and such as DL 6672A, DL6638A, and DL6663A, available from

Dow Chemical Company), (2) ethylenevinylacetate latex (such as Airflex 400, available from Air Products and Chemicals Inc.), and (3) vinyl acetate-acrylic copolymer latexes (such as synthemul 97-726, available from Reichhold Chemical Inc, Resyn 25 -1110 and Resyn 25-1140, available from National Starch Company, and RES 3103 available from Unocal Chemicals; (f) maleic anhydride and maleic acid containing polymers, such as (1) styrene-maleic anhydride copolymers (such as that available as Scripset from Monsanto, and the SMA series available from Arco), (2) vinyl alkyl ether-maleic anhydride copolymers, wherein alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl, and the like (such as vinyl methyl ether-maleic anhydride copolymer #173, available from Scientific Polymer Products), (3) alkylene-maleic anhydride copolymers, wherein alkylene has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl, and the like (such as ethylene-maleic anhydride copolymer #2308, available from Poly Sciences Inc., also available as EMA from Monsanto Chemical Company), (4) butadiene-maleic acid copolymers (such as #07787, available from Poly Sciences Inc.), (5) vinylalkylether-maleic acid copolymers, wherein alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl, and the like (such as vinylmethylether-maleic acid copolymer, available from GAF Corporationas Gantrez S-95), and (6) alkyl vinyl ether-maleic acid esters, wherein alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably from 1 to about 20 carbon atoms, more preferably from 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl, and the like (such as methyl vinyl ethermaleic acid ester #773, available from Scientific Polymer Products); (g) acrylamide containing polymers, such as (1) poly (acrylamide) (such as #02806, available from Poly Sciences Inc.), (2) acrylamide-acrylic acid copolymers (such as #04652, #02220, and #18545, available from Poly Sciences Inc.), and (3) poly (N,N-dimethyl acrylamide) (such as #004590, available from Poly Sciences Inc.); and (h) poly (alkylene imine) containing polymers, wherein alkylene has two (ethylene), three (propylene), or four (butylene) carbon atoms, such as (1) poly(ethylene imine) (such as #135, available from Scientific Polymer Products), (2) poly(ethylene imine) epichlorohydrin (such as #634, available from Scientific Polymer Products), and (3) alkoxylated poly (ethylene imine), wherein alkyl has one (methoxylated), two (ethoxylated), three (propoxylated), or four (butoxylated) carbon atoms (such as ethoxylated poly (ethylene imine #636, available from Scientific Polymer Products); and the like, as well as blends or mixtures of any of the above, with starches and latexes being particularly preferred because of their availability and applicability to paper. Any mixtures of the above ingredients in any relative amounts can be employed.

If present, the binder can be present within the coating in any effective amount; typically the binder and the cationic sulfur compound are present in relative amounts of from about 10 parts by weight binder and about 90 parts by weight cationic sulfur compound to about 50 parts by weight binder and about 50 parts by weight cationic sulfur compound, although the relative amounts can be outside of this range.

In addition, the coating of the recording sheets of the present invention can contain optional filler components. Fillers can be present in any effective amount, and if present, typically are present in amounts of from about 1 to about 60 percent by weight of the coating composition. Examples of filler components include colloidal silicas, such as Syloid 74, available from Grace Company (preferably present, in one embodiment, in an amount of about 20 weight percent), titanium dioxide (available as Rutile or Anatase from NL Chem Canada, Inc.), hydrated alumina (Hydrad TMC-HBF, Hydrad TM-HBC, available from J. M. Huber Corporation), barium sulfate (K. C. Blanc Fix HD80, available from Kall Chemie Corporation), calcium carbonate (Microwhite Sylacauga Calcium Products), high brightness clays (such as Engelhard Paper Clays), calcium silicate (available from J. M. Huber

Corporation), cellulosic materials insoluble in water or any organic solvents (such as those available from Scientific Polymer Products), blend of calcium fluoride and silica, such as Opalex-C available from Kemira.O.Y, zinc oxide, such as Zoco Fax 183, available from Zo Chem, blends of zinc sulfide with barium sulfate, such as Lithopane, available from Schteben Company, and the like, as well as mixtures thereof. Brightener fillers can enhance color mixing and assist in improving print-through in recording sheets of the present invention.

The coating containing the cationic sulfur compound is present on the substrate of the recording sheet of the present invention in any effective thickness. Typically, the total thickness of the coating layer is from about 1 to about 25 microns and preferably from about 2 to about 10 microns, although the thickness can be outside of these ranges.

The cationic sulfur compound or the mixture of cationic sulfur compound, optional binder, and/or optional filler can be applied to the substrate by any suitable technique, such as size press treatment, dip coating, reverse roll coating, extrusion coating, or the like. For example, the coating can be applied with a KRK size press (Kumagal Riki Kogyo Co., Ltd., Nerima, Tokyo, Japan) by dip coating and can be applied by solvent extrusion on a Faustel Coater. The KRK size press Is a lab size press that simulates a commercial size press. This size press is normally sheet fed, whereas a commercial size press typically employs a continuous web. On the KRK size press, the substrate sheet is taped by one end to the carrier mechanism plate. The speed of the test and the roll pressures are set, and the coating solution is poured into the solution tank. A 4 liter stainless steel beaker is situated underneath for retaining the solution overflow. The coating solution is cycled once through the system (without moving the substrate sheet) to wet the surface of the rolls and then returned to the feed tank, where it is cycled a second time. While the rolls are being "wetted", the sheet is fed through the sizing rolls by pressing the carrier mechanism start button. The coated sheet is then removed from the carrier mechanism plate and is placed on a 12 inch by 40 inch sheet of 750 micron thick Teflon for support and is dried on the Dynamic Former drying drum and held under restraint to prevent shrinkage. The drying temperature is approximately 105.degree. C. This method of coating treats both sides of the substrate simultaneously.

In dip coating, a web of the material to be coated is transported below the surface of the liquid coating composition by a single roll in such a manner that the exposed site is saturated, followed by removal of any excess coating by the squeeze rolls and drying at 100.degree. C. in an air dryer. The liquid coating composition generally comprises the desired coating composition dissolved in a solvent such as water, methanol, or the like. The method of surface treating the substrate using a coater results in a continuous sheet of substrate with the coating material applied first to one side and then to the second side of this substrate. The substrate can also be coated by a slot extrusion process, wherein a flat die is situated with the die lips in close proximity to the web of substrate to be coated, resulting in a continuous film of the coating solution evenly distributed across one surface of the sheet, followed by drying in an air dryer at 100.degree. C.

Recording sheets of the present invention can be employed in ink jet printing processes. One embodiment of the present invention is directed to a process which comprises applying an aqueous recording liquid to a recording sheet of the present invention In an imagewise pattern. Another embodiment of the present invention is directed to a printing process which comprises (1) incorporating Into an ink jet printing apparatus containing an aqueous ink a recording sheet of the present invention, and (2) causing droplets of the ink to be ejected in an imagewise pattern onto the recording sheet, thereby generating images on the recording sheet. Ink jet printing processes are well known, and are described in, for example, U.S. Pat. No. 4,601,777, U.S. Pat. No. 4,251,824, U.S. Pat. No. 4,410,899, U.S. Pat. No. 4,412,224, and U.S. Pat. No. 4,532,530, the disclosures of each of which are totally incorporated herein by reference. In a particularly preferred embodiment, the printing apparatus employs a thermal ink jet process wherein the ink in the nozzles is selectively heated in an imagewise pattern,

thereby causing droplets of the ink to be ejected in imagewise pattern.

The recording sheets of the present invention can also be used in any other printing or imaging process, such as printing with pen plotters, handwriting with ink pens, offset printing processes, or the like, provided that the ink employed to form the image is compatible with the ink receiving layer of the recording sheet.

Specific embodiments of the invention will now be described in detail. These examples are intended to be illustrative, and the invention is not limited to the materials, conditions, or process parameters set forth in these embodiments. All parts and percentages are by weight unless otherwise indicated.

The optical density measurements recited herein were obtained on a Pacific Spectrograph Color System. The system consists of two major components, an optical sensor and a data terminal. The optical sensor employs a 6 inch integrating sphere to provide diffuse illumination and 8 degrees viewing. This sensor can be used to measure both transmission and reflectance samples. When reflectance samples are measured, a specular component may be included. A high resolution, full dispersion, grating monochromator was used to scan the spectrum from 380 to 720 nanometers. The data terminal features a 12 inch CRT display, numerical keyboard for selection of operating parameters and the entry of tristimulus values, and an alphanumeric keyboard for entry of product standard information.

EXAMPLE I

Plain paper sheets (Simpson alkaline sized, carrying no surface treatments, obtained from Simpson Paper Co., Kalamazoo, Mich.) measuring 8.5.times.11 inches were treated with solutions comprising 2 percent by weight of a cationic sulfur compound and 98 percent of a solvent (specifically identified for each compound in the table below; meOH=methanol; ratios are by weight) via dip coating and dried in air at 100.degree. C. Subsequent to treatment, each paper sheet had deposited on each side thereof about 100 milligrams of the cationic sulfur compound. The treated papers, as well as sheets of the Simpson paper which had not been treated with a cationic sulfur compound, were incorporated into a Xerox.RTM.4020 ink jet printer, and full color prints were generated on each sheet by the printer. The optical density of the cyan, magenta, yellow, and black images were measured. Subsequently, the images were tested for water resistance by washing them at 50.degree. C. for 2 minutes with water followed by again measuring the optical densities of the images. The results were as follows:

Cmpd.	Black Bef.	Black Aft.	Black WF	Cyan Bef.	Cyan Aft.	Cyan WF	Magenta Bef.	Magenta Aft.	Magenta WF	Yellow Bef.	Yellow Aft.	Yellow WF
none	1.11	0.74	67	0.97	0.72	74	1.01					

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                          0.48
                             48 0.75
                                   0.62
                                      83
1    1.10
        1.10
           100
              1.19
                 1.19
                    100
                       0.95
                          0.95
                             100
                                0.95
                                   0.95
                                      100
2    1.29
        1.23
           95 1.18
                 1.04
                    88 1.04
                          0.78
                             75 0.82
                                   0.84
                                      102
3    1.26
        0.95
           75 1.04
                 0.81
                    78 0.99
                          0.50
                             51 0.75
                                   0.65
                                      87
4    1.19
        1.02
           86 1.04
                 1.00
                    96 0.93
                          0.67
                             72 0.76
                                   0.73
                                      96
5    1.28
        1.13
           88 1.10
                 0.88
                    80 0.96
                          0.60
                             63 0.83
                                   0.78
                                      94
6    1.23
        0.97
           79 1.03
                 0.91
                    88 0.94
                          0.58
                             62 0.75
                                   0.72
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optical density and waterfastness of coated papers printed with Xerox .RTM. 4020 ink jet printer

#	Compound	Solvent
1	3,6-(dimethyl-2-(4-dimethyl amino phenyl) benzothiazolium bromide (Aldrich 15,242-0)	meOH
2	3-(carboxymethyl) benzo thiazolium bromide (Aldrich 37,163-7)	H.sub.2 O
3	3-ethyl-2-(2-hydroxy-1-propenyl)-benzothiazolium chloride (Aldricj 29,365-2)	50:50 H.sub.2 O/meO H
4	dimethyl(2-methoxy-5-nitrobenzyl) sulfonium bromide (Aldrich 85,775-0)	50:50 H.sub.2 O/meO H
5	trimethyl sulfonium methyl sulfate (Aldrich 30,359-3)	H.sub.2 O
6	p-xylenebis(tetra hydro thiophenium chloride) (Aldrich 37,708-2)	meOH

As the data indicate, the sheets treated with the cationic sulfur compounds generally exhibited superior water fastness compated to those sheets not treated with a cationic compound.

Other embodiments and modifications of the present invention may occur to those skilled in the art subsequent to a review of the information presented herein; these embodiments and modifications, as well as equivalents thereof, are also included within the scope of this invention.

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